

Polymer with tetrazolic pendant groups. Interaction between the heterocyclic groups and heavy metals

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ABSTRACT

The interaction between a polymer with tetrazolic pendant groups, and heavy metals (Pb(II) or Cd(II)) was studied. The product resulting from these interactions was characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy coupled with an energy dispersive X ray fluorescence. From FT-IR analysis we can conclude that the interaction between tetrazole rings and divalent metals is a combination of *N*-coordination and salt formation. As results of these interactions 1.3 mmol of Pb(II) or 1.5 mmol of Cd(II) per gram of polymer are removed from aqueous solution. The metals as well as the organic material can be recuperated from the solid by pH shifting; indeed the polymer can be reused.

KEYWORDS: tetrazole, heterocycle pendant group polymer, metal interaction

ABBREVIATIONS

DSC, differential scanning calorimetry; DMF, dimethylformamide; DMSO, dimethylsulfoxide; FT-IR, Fourier transform infrared spectroscopy;

ICP-OES, Inductively Coupled Plasma – Optical Emission Spectroscopy; *MFPAN*, Modified Fiber Polyacrylonitrile; *MFPAN-Cd*, precipitate obtained from interaction of *MFPAN* and Cd(II); *MFPAN-Cu*, precipitate obtained from interaction of *MFPAN* and Cu(II); *MFPAN-Pb*, precipitate obtained from interaction of *MFPAN* and Pb(II); *MFPAN-R*, Recovered *MFPAN* after interaction with metals; PAN, polyacrylonitrile; SEM-EDX, scanning electron microscopy coupled with an energy dispersive X ray fluorescence; Tg, glass transition temperature; TGA, thermogravimetric analysis

INTRODUCTION

Heterocycles like pyridines, pyrazidines, 1,2,4,5-tetrazines; 1,2,4-triazoles; 1,3,4-thiadiazazoles; 1,3,4-oxadiazoles and imidazoles (among others), are well known by their coordinating interaction with different metals [1-3].

In the past years many authors worked on the synthesis of autostructured coordination polymers between organic ligands and some metals, not only by their topological interest but because of their potential application in several fields, like catalysis, gas storage and ionic exchange, focusing on *N*-heterocyclic ligands due to their structural rigidity and flexible coordination ways [4].

In particular, molecules with tetrazole rings are capable of yielding two- and three-dimensional coordination polymers with Cu(II) [5-7]. On the

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other hand, He *et al.*, reported that the 5-methyltetrazole acts as a tridentate ligand forming a 3D network, in which the skeleton framework has Cu(I) and Cu(II) octacoordinated by six tetrazole units, via *N*-2, *N*-3 and *N*-4 [8].

On the other hand it is well known that it is safe and easier to modify polymers than to synthesize them starting from the corresponding monomers. In this field, we have described the synthesis of terpolymers with oxadiazolic, oxazolic or benzoimidazolic pendant groups based on polymer-analog transformation, for use as graver-packed carrier fluid, completion fluid or fracturing fluid [9-11].

In a previous work we reported the chemical modification of industrial copolymer with a high proportion of acrylonitrile (91.5%) applying 1,3-dipolar cycloaddition reaction. The nitrile groups (dipolarophiles) with ammonium azide generated *in situ* (dipole), originated a copolymer having tetrazolic pendant groups; this copolymer was used to remove Cu(II) from aqueous solutions [12]. Taking into consideration the above remarks, we studied the possibility of this copolymer, with tetrazole ring as pendant groups, interacting with Cd(II) and Pb(II). The product of tetrazoles and heavy metal interaction was studied by FT-IR, TGA, DSC and SEM-EDX.

MATERIALS AND METHODS

General methods

All reagents were of analytic grade or better. Standard solutions of Pb(II) and Cd(II) were made by dissolving Pb(NO₃)₂ (Sigma-Aldrich) and CdCl₂·2½H₂O (Sigma-Aldrich) in milliQ water (Millipore). The amount of metal was determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000DV) and calibration was made with a standard set prepared from a multimetallic solution with certified trazability. Peak integration was made by Multicomponent Spectral Fitting algorithm [13].

FT-IR Spectra were made on a Shimadzu IR Affinity-1 between 400 and 4000 cm⁻¹, using KBr disc. SEM-EDX was performed on a Philips XL30ESEM. TGA and DSC were performed on a STD-Q600 analyzer (TA Instrument USA). The temperature range ramp was from 25 °C to 1500 °C

at a heating rate of 2 °C min⁻¹, using sample weights of 4.0-6.0 mg. A nitrogen flux rate of 20.0 mL min⁻¹ was applied.

Metal-polymer precipitation

Interaction between *MFPAN* and metal was performed adding increasing volumes of metal solution to a fixed quantity of polymer solution and then, water to reach the same final volume. The mass ratio needed to produce precipitate was previously estimated for each metal. Thus, experiments were carried out in lower and larger ratios, with the aim to have experiments with and without precipitate. Nine experiments were done for each metal, using the following procedure.

To a solution of *MFPAN* (2.25 mL, 1.91 mg mL⁻¹) a certain amount of lead or cadmium solution was added, (2.39 mg mL⁻¹ or 0.50 mg mL⁻¹), and then diluted with water to 3 mL. This procedure was repeated with different volumes of metal solution (0.075 to 0.75 mL for lead, 0.08 to 1.50 mL for cadmium). The homogenized mixtures were left at room temperature for 20 minutes and the pH was registered (being between 4.5 and 5.5 in all cases). Precipitates were separated by centrifugation, and the remaining metal in solution was determined by ICP-OES. Once dried, the precipitates were analyzed by SEM-EDX, TGA, DSC and FT-IR.

MFPAN-Pb: This compound was isolated as a white gelatinous solid, which becomes hard after being dried. FT-IR 3742-2361 (broad), 2245, 1717, 1670, 1474, 964 cm⁻¹. *Anal.* Found: C, 24.48; H, 2.93; N, 27.86; ash, 38.27.

MFPAN-Cd: This compound was isolated as a white gelatinous solid, which becomes hard when dried. FT-IR 3757-2415 (broad), 2247, 1722, 1666, 1477, 964 cm⁻¹. *Anal.* Found: C, 29.55; H, 3.75; N, 32.57; ash 19.50.

Metal uptake, metal release and polymer recovery

The amounts of metal in supernatant and precipitate were calculated using equations 1 and 2.

$$1: m_s (mg) = \frac{C_s \times V}{1000}$$

$$2: m_p (mg) = \frac{V \times (C_0 - C_s)}{1000}$$

V is the final volume of solution in milliliters

C_0 is the concentration of stock standard solution of metal in mg/L

C_s is the concentration of metal in the supernatant in mg/L.

The precipitates obtained by centrifugation were treated with HCl (5 mL, 0.1 N). The mixture was vigorously shaken for ten minutes and then centrifuged. The solid was separated (*MFPAN-R*) and the metal content was analyzed by ICP-OES on the liquid fraction (18.50% of lead in *MFPAN-Pb* and 14.90% of cadmium in *MFPAN-Cd*). Due to the insolubility of *MFPAN-R* in water, it had to be dissolved by treatment with potassium hydroxide (3 mL, 0.1 M) and then neutralized with HCl (1 N). This solution of recovered polymer is suitable to reuse as a cation removal agent.

RESULTS AND DISCUSSION

Interaction between the copolymer with tetrazolic pendant groups (*MFPAN*) and Pb or Cd produced a gelatinous precipitate beyond a critical concentration of cations (*MFPAN-Pb* or *MFPAN-Cd*). Precipitation appeared when the metal/polymer ratio surpassed a certain threshold. Below this threshold precipitation did not take place and the amount of metal in solution was exactly the amount added. Above the threshold, precipitation occurred, but the amount of metal in the precipitate continued to be invariable and independent of the quantity of metal added, and in this case only the concentration in the supernatant increased.

The thresholds found for precipitation are shown in Table 1, and when expressed in mol/mg, suggested a pseudo-stoichiometry between metal and polymer. Taking into account the initial composition of *MFPAN*, we could estimate a 6:1 molar relationship between tetrazole and metal. The solids obtained were analyzed and compared with the material derived from copper interaction (*MFPAN-Cu*), previously described [12].

MFPAN-Pb and *MFPAN-Cd* were highly insoluble in a series of solvents, even in DMF and DMSO. Once dried, these materials were analyzed and the elemental analyses showed a high content of ashes, confirming the presence of metals (See Experimental). In order to reuse the polymer, the precipitates obtained by centrifugation were treated with hydrochloric acid. The solid was separated (*MFPAN-R*) and the metal content on the liquid fraction was analyzed by ICP-OES (See MATERIALS AND METHODS). The complete process is depicted in Figure 1.

The superficial differences between *MFPAN* and *MFPAN-Pb* or *MFPAN-Cd* were analyzed using SEM. From these micrographs it can be observed that the surface of *MFPAN* appears like smooth flakes while *MFPAN-Cd* is rougher and seems to be more compact. EDX Spectrum of *MFPAN-Pb* is shown in Figure 2(a), and the characteristic atomic lines corresponding to the cation present in the precipitate can be observed. Figure 2(b) shows similar information for *MFPAN-Cd*.

Thermal analysis of *MFPAN-Pb* shows a slight loss of mass of 4.9%, which could be assigned to a loss of water that was entrapped in the polymer. Two main mass decreases are observed at 300 °C (32.9%) and 1010 °C (12.9%), leaving a residue of 25.6% at 1500 °C. *MFPAN-Cd* also shows an initial loss of mass associated with the loss of residual water (1.9%) and a main mass decrease at 310 °C (33.3%) followed by nonspecific loss. It is important to notice that the latter material (*MFPAN-Cd*) even at 1500 °C does not reach the plateau, leaving a residue of 26.9%.

From TGA experiments on *MFPAN-R* and *MFPAN* we could observe that the decomposition temperature of *MFPAN-R* (280 °C) is 20 °C greater than that of *MFPAN* (260 °C), resulting in *MFPAN-R* being slightly more stable than *MFPAN*. On other hand, *MFPAN-R* does not show

Table 1. Thresholds for metal-polymer precipitation in mg/mg and mmol/mg.

Precipitate	mg Metal/mg Polymer	mmol Metal/mg Polymer
<i>MFPAN-Pb</i>	0.27 ± 0.01	0.0013 ± 0.0001
<i>MFPAN-Cd</i>	0.17 ± 0.03	0.0015 ± 0.0003
<i>MFPAN-Cu</i> ¹⁵	0.096 ± 0.004	0.0015 ± 0.0001

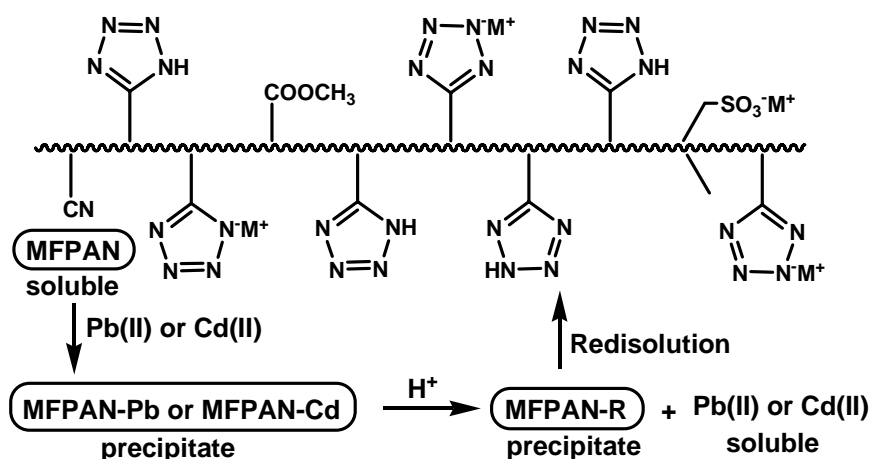


Figure 1. Complete process for metal capture, metal recovery and polymer reutilization.

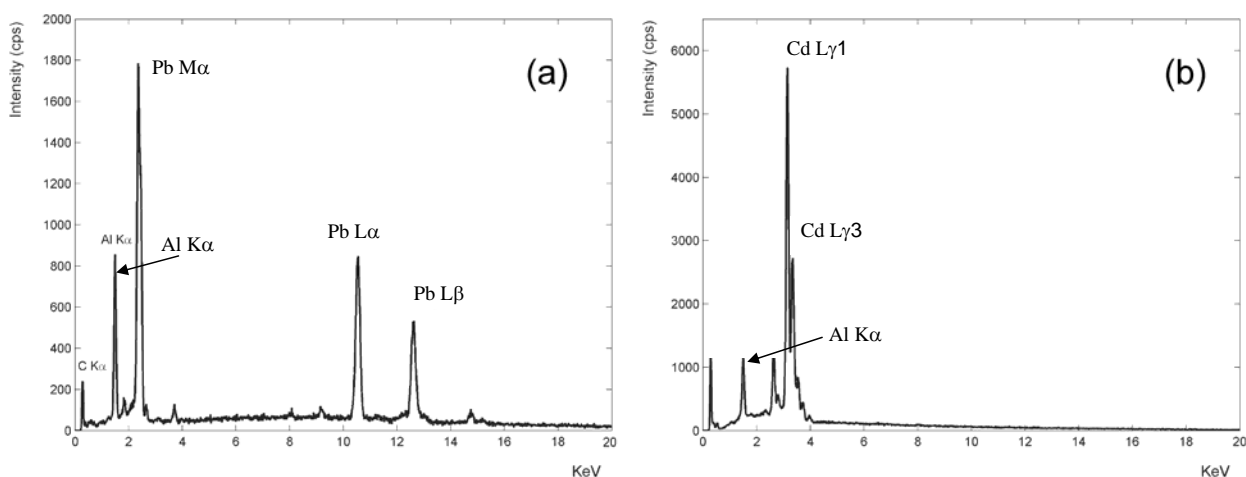


Figure 2. EDX Spectrum for *MFPAN-Pb* (a) and *MFPAN-Cd* (b).

an initial loss of water as is observed for *MFPAN*, *MFPAN-Pb* and *MFPAN-Cd*, and so we can conclude that the amount of retained water in this material is negligible. In order to determinate the glass transition of *MFPAN-Pb* and *MFPAN-Cd*, we performed DSC experiments (See Table 2). From these data we can conclude that both the products are hard solids at room temperature and this can be interpreted as a consequence of the metal-polymer interaction.

The FT-IR spectra of *MFPAN-Pb* and *MFPAN-Cd* were analyzed and compared with those of *MFPAN* and *MFPAN-Cu*. All the materials showed bands corresponding to tetrazolic ring and nitrile groups and were very similar. From this data we can

Table 2. Observed glass transition temperatures (T_g) for *MFPAN-Pb* and *MFPAN-Cd*.

Precipitate	T _g
<i>MFPAN-Pb</i>	115.3 °C
<i>MFPAN-Cd</i>	128.4 °C

conclude that the integrity of the polymer is not compromised by its interaction with the metals. A band around 2250 cm⁻¹ from unconverted nitrile groups was detected, and also a C=N stretching band at 1650 cm⁻¹ from tetrazole units, the last signal is consistent with the stretching for complete polyacrylonitrile conversion [14]. The broad band

at 2400-3600 cm^{-1} could be attributed to the acidic *N*-H plus the *O*-H stretching of water trapped into the polymer.

Usually, *NH* heterocycles show a band pattern between 3000 and 1700 cm^{-1} which is attributed to proton polarizability of the hydrogen bonds in *NH...N - N...HN* semi-salt equilibrium [15, 16]. These band patterns depend on the ring nature, and are caused by Fermi resonance of $\nu(\text{NH})$ stretching vibration with the overtone of the ring vibration. The lowest wave number band of this range is characteristic for every studied *NH* heterocycle. It is important to note that this particular band is not observed when the salt is completely formed. In our case, although we cannot observe all tetrazolic ring patterns, the presence of the lowest wave number band at 1961 cm^{-1} allows the consideration as an evidence that *MFPAN* must be a semisalt. The semi-salt nature of *MFPAN* was confirmed by EDX, which showed the presence of calcium and sodium in this polymeric material.

Comparing the FT-IR spectrum for *MFPAN* with those of the three precipitates, we observe the

disappearance of the 1961 cm^{-1} band, and so we inferred that one of the metal-polymer interactions is the salt formation. This interaction of divalent cation with tetrazolic rings produces an electrostatic crosslinking between the chains of the polymer, and then the precipitate is formed.

Tetrazole group can act as carboxylic acid and also their nitrogen atoms are capable of coordinating with different metals. So, the nature of *MFPAN-metal* interaction could be more complex than a salt formation. When tetrazole ring was complexed with metals, several changes on its FT-IR spectrum were observed. Tetrazoles complexed with Cu(II) showed major changes in the 900-1100 cm^{-1} region, with new bands and new maxima [15, 16], and weak to medium intensity bands between 1200-1300 cm^{-1} region became more intense on metal complexation. Moreover, bands at 1270-1300 cm^{-1} and 1450-1500 cm^{-1} were shifted 30 cm^{-1} and 20 cm^{-1} , respectively, to higher frequency by formation of the complex. *MFPAN-Pb*, *MFPAN-Cd* and *MFPAN* show almost the same band pattern in the 900-1500 cm^{-1} zone, which could indicate that there is no coordination between *MFPAN* and divalent cations.

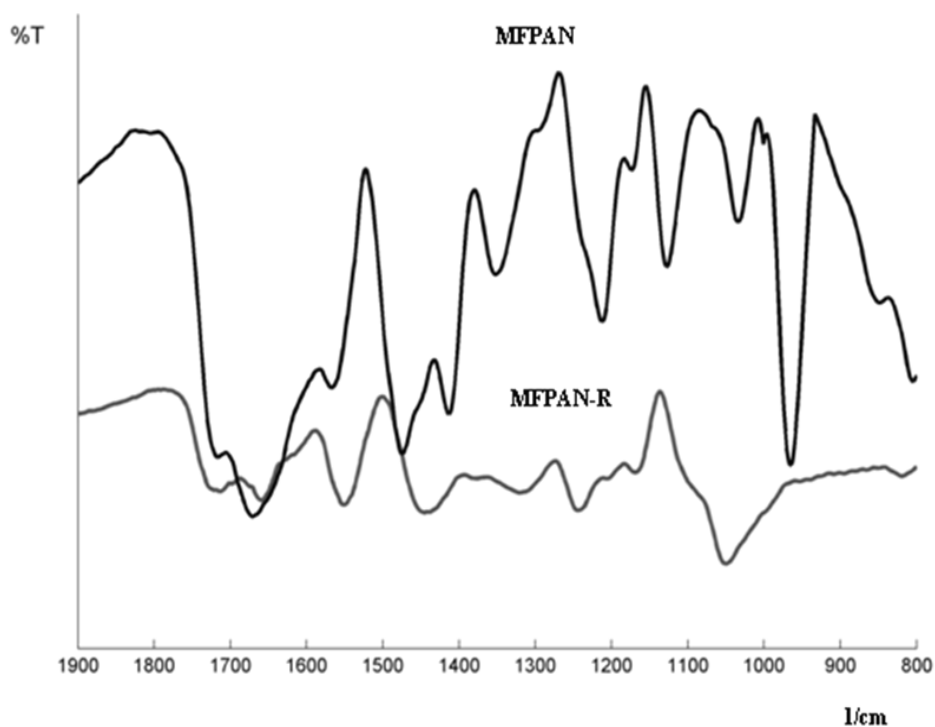


Figure 3. Detail of FT-IR spectra of *MFPAN* and *MFPAN-R*.

As it was mentioned before, *MFPAN* already contains divalent cations. Due to the different solubilities of *MFPAN-R* and *MFPAN* (See Experimental), and taking into account the different retention of water, already mentioned, we can conclude that they cannot be exactly the same polymer. From the FT-IR analysis of *MFPAN-R* and *MFPAN* spectra (Figure 3), we can conclude that *MFPAN-R* spectrum is very similar to the polyvinyltetrazole reported in literature [14], and from comparison of the two spectra we can affirm that the main difference between *MFPAN-R* and *MFPAN* is the protonation degree. Bands at 1475 and 1357 cm^{-1} of *MFPAN* (which could be assigned to C=N and N-N stretching) are shifted 31 and 36 cm^{-1} respectively for *MFPAN-R* (1444 and 1321 cm^{-1}). As it was mentioned earlier, this behavior is consistent with that observed for tetrazoles when coordinated with Cu(II) [17].

On the other hand, stretching-deformation vibrations of the tetrazole ring, which appear in the 900-1100 cm^{-1} , suffer changes with new maxima when complexed. *MFPAN* showed a strong absorption at 966 cm^{-1} , which is shifted to 1051 cm^{-1} for *MFPAN-R*. From this data we can conclude that the spectrum of *MFPAN* shows no difference from *MFPAN-Cu*, *MFPAN-Pb* and *MFPAN-Cd* because *MFPAN* has already a coordinated counterion, Ca(II) according to EDX data. The observed differences between the FT-IR of *MFPAN-R*, *MFPAN-Pb* and *MFPAN-Cd* indicated that the polymer-metal interaction includes a coordination effect in addition to the salt formation.

Each gram of polymer is capable of precipitating 270 mg of Pb(II) or 170 mg of Cd(II), which represents a molar tetrazole:metal relationship of 6:1. From FT-IR analysis we can conclude that the interaction between tetrazole rings and divalent metals are a combination of *N*-coordination and salt formation. The 6:1 molar relationship suggested that two heterocycles form the salt with the cation, while the other four heterocyclic rings are probably acting as coordination agents.

CONCLUSION

The employed methodology for metal recovery is particularly interesting for many reasons. First of all,

it seems to be suitable for the treatment of industrial effluents with high content of heavy metals, which must be treated before disposal to the environment. Also, the low cost and re-use capacity of the copolymer makes its use consistent with the needs of the industry and favors its application. Finally, the *MFPAN* was prepared from a residual polymer and its conversion can contribute to reduce the volume of residues with large persistence in the environment and also to metal recovery from waste waters at the same time.

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